

## PATENT SPECIFICATION

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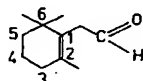
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(54) NOVEL FLAVORING AND FRAGRANCE COMPOSITIONS  
 CONTAINING ALPHA-SUBSTITUTE ACETALDEHYDE  
 AND METHODS OF MAKING SAME

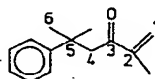
(71) We, INTERNATIONAL FLAVORS & FRAGRANCES INC., a corporation of the State of New York in the United States of America having an office at 521, West 57th Street, New York, New York 10019, U.S.A., do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The present invention relates to the use of 2,6,6-trimethyl-1-cyclohexen-1-yl acetaldehyde (hereinafter called "beta-cyclohomocitral") having the structure

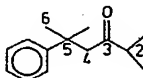


and novel compositions using such beta-cyclohomocitral taken alone, or taken together with at least one of the compounds:

2,5-dimethyl-5-phenyl hexen-1-one-3 (hereinafter called "Damascol"); having the structure

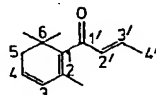


2,5-dimethyl-5-phenyl hexanone-3 (hereinafter called "Damascol-4") having the structure



and or

2,6,6-trimethyl-1-(but 2'-en-1'-oyl)-1,3-cyclohexadiene (hereinafter called "Damascenone") having the structure



(which may alternatively be named as 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene)

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to alter, modify or enhance the flavor and/or aroma of consumable materials, such as foodstuffs, foodstuff flavors, perfume compositions, perfumed articles, tobaccos, tobacco flavors, chewing gums, chewing gum flavors, medicinal products and medicinal product flavors.

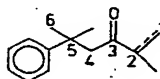
The organoleptic properties of Damascenone are set forth in Swiss Patent 520,479 issued on May 12, 1972.

One aspect of our invention is that novel solid and liquid foodstuff and flavoring compositions having fruity, woody and tea aromas and woody-tea and fruity-tobacco tastes, novel perfume compositions having woody, camphoraceous, green, earthy, floral and rosey notes; as well as novel tobacco flavoring compositions having sweet, rich-tobacco, floral fruity, green, woody, "damascenone-like" and earthy notes may be provided by the utilization of beta-cyclohomocitral in foodstuffs, chewing gums, medicinal products, perfume compositions, perfumed articles, colognes and tobaccos as well as tobacco substitutes.

According to another aspect of our invention, novel perfume compositions and perfumes having highly intense and natural-like rosey notes and novel perfumed articles having intense rosey aromas with, if desired, woody, green and earthy notes may be provided by the utilization of mixtures of (i) one or both of the phenyl C<sub>6</sub> ketones, "Damascol-4" and "Damascol" and (ii) beta-cyclohomocitral in perfumes, perfumed articles, perfume compositions and colognes.

It has also been discovered by us that the organoleptic effect obtained when using the combination of one or both of the foregoing phenyl C<sub>6</sub> ketones and beta-cyclohomocitral is more than merely additive of the individual organoleptic properties of each of the phenyl C<sub>6</sub> ketones and beta-cyclohomocitral; that the effect is described as "synergistic".

Generically the structure of the phenyl C<sub>6</sub> ketones used in our invention is as follows:



wherein the dashed line indicates that the  $\Delta$  1,2 bond may either be a carbon-carbon single bond or a carbon-carbon double bond.

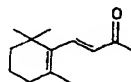
According to another aspect of our invention, novel solid and liquid foodstuff, chewing gum, medicinal product, and flavoring composition having rosey, fruity, woody and tea aromas and woody-tea and fruity-tobacco tastes, novel perfume compositions having rosey, woody, camphoraceous, green, earthy notes; as well as novel tobacco flavoring compositions having sweet, rich-tobacco, floral, fruity, green, woody and earthy notes may be provided by the utilization of mixtures of "Damascenone" and beta-cyclohomocitral in foodstuffs, perfume compositions, perfumed articles, colognes and tobaccos as well as tobacco substitutes.

It has also been discovered by us that the organoleptic effect obtained when using the combination of Damascenone and beta-cyclohomocitral is more than merely additive of the individual organoleptic properties and strength of each of Damascenone and beta-cyclohomocitral; that the effect can be described as "synergistic."

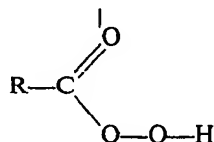
According to another aspect of our invention, the beta-cyclohomocitral so useful, may be produced, preferably, by processes which comprise either (a) a reaction carried out in two steps, namely firstly oxidating beta-ionone with either performic acid, peracetic acid or perpropionic acid to form beta-ionone enol ester and, secondly, hydrolyzing the beta-ionone enol ester in the presence of base (either aqueous or alcoholic) to form the desired beta-cyclo-homocitral or (b) a single stage reaction, namely oxidizing beta-ionone with hydrogen peroxide in the presence of inorganic base. In this connection, see copending Application Nos. 26513/78 (Serial No. ) and 26514/78 (Serial No. 1,530,466) divided herefrom.

More specifically, the first alternative (a) comprises the steps of:

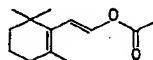
(1) Reacting beta-ionone having the formula:



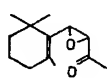
in the absence of dimethyl formamide with a peralkanoic acid having the formula:



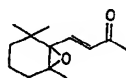
(wherein R is hydrogen, methyl or ethyl) to form beta-ionone enol ester having the formula:



and not the expected beta-ionone epoxide having one of the formulae:



and/or



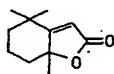
; and

(2) hydrolyzing the beta-ionone enol ester in the presence of base (aqueous or alcoholic) to form beta-cyclohomocitral.

Insofar as concerns the oxidation reaction in the two stage reaction (a) where peralkanoic acids are used as the oxidizing agents, the reaction is preferably carried out in the presence of a buffer such as an alkali metal salt of a lower alkanolic acid or an alkali metal carbonate with a lower alkanolic acid such as propionic acid acetic acid or formic acid with the following provisos:

(i) The reaction is preferably carried out at temperatures of from 15°C up to about 75°C. Lower temperatures result in slower and less complete reaction and higher temperatures than 75°C result in lower yields of the desired product and significantly higher percentages of by-products. The most preferred temperature of reaction is 25°C.

(ii) A slight molar excess (from 10 to 15 percent) of peracetic acid gives a slightly higher yield of product. A large excess (about 200 percent), however, results in the formation of dihydroactinodiolide having the structure:



in about 30—35 percent yield when no buffer (e.g., potassium acetate) is present in the reaction mass;

(iii) Where potassium carbonate is substituted for potassium acetate as a buffer, the yield of product obtained is substantially the same;

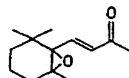
(iv) On the other hand, a slightly lower yield of product is obtained by substituting sodium acetate for potassium acetate as the buffer;

(v) Substitution of formic acid for acetic acid in the reaction mass gives rise to a lower yield of product.

(vi) Any solvent inert to the action of peralkanoic acids may be used in this first oxidation reaction using alkanolic acids. For instance, the use of cyclohexane or chloroform as a solvent does not have an appreciable effect on the yield of product;

(vii) Omission of the buffer (i.e., thus performing the reaction under strongly acidic conditions) results in an incomplete reaction, lower yield and greater quantity of by-product(s);

(viii) The use of dimethyl formamide as solvent results in the exclusive formation of beta-ionone epoxide having the structure:



in about 70—75% yield and, accordingly, the presence of dimethyl formamide must be avoided;

(ix) The use of monoperphthalic acid (formed *in situ* from phthalic anhydride and hydrogen peroxide) yields beta-ionone epoxide in 60–70 percent yield. The use of perbenzoic acid in place of a peralkanoic acid has also been used to make beta-ionone epoxide R. Yyes, et al., *Helv. Chim. Acta*, 29, 880 (1946).

It may be concluded that a peralkanoic acid such as peracetic acid in slight excess in the presence of a buffer system, preferably composed of acetic acid/potassium acetate is the preferred way to oxidize beta-ionone at 25°C to the corresponding enol acetate.

The beta-ionone enol ester preferably is hydrolyzed by 10 percent alkali metal hydroxide (e.g., potassium hydroxide, lithium hydroxide or sodium hydroxide) in admixture with 50 percent aqueous methanol, although other mild hydrolysis conditions (such as aqueous potassium carbonate, sodium carbonate or lithium carbonate solution) may also be used. As a result of the hydrolysis, beta-cyclohomocitral is formed.

The resultant reaction product, beta-cyclohomocitral may then be refined according to standard techniques, e.g. preparative gas chromatography, extraction, distillation and the like as further exemplified herein.

Insofar as concerns the oxidation reaction in the single stage reaction (b) where hydrogen peroxide (in the presence of inorganic base) is used as the oxidizing agent, the strength of hydrogen peroxide used is from about 10 percent up to about 50 percent, and the inorganic base used may be alkali metal hydroxide or alkali metal carbonate such as sodium carbonate, potassium carbonate, lithium carbonate, sodium hydroxide, potassium hydroxide or lithium hydroxide; preferably sodium hydroxide. The mole ratio of hydrogen peroxide: beta-ionone is preferably from about 1.1:1 up to about 3:1.

The aforementioned processes are specific to beta-ionone. As further exemplified *infra*, when the reaction conditions of this process are applied to alpha-ionone, as opposed to beta-ionone, epoxide formation occurs and neither a substantial amount of enol acetate nor isomers of beta-cyclohomocitral are formed.

The 2,2,6-trimethyl-1-cyclohexen-ylacetaldehyde (or beta-cyclohomocitral) of our invention is capable of modifying, altering, enhancing, supplying and/or potentiating certain flavor and aroma notes usually lacking in many fruit and red berry flavors as well as tobacco flavors heretofore provided. Furthermore, the betacyclohomocitral of our invention is capable of supplying certain fragrance notes usually lacking in many perfumery materials, for example, petitgrain fragrances, rose fragrances, muguet fragrances and floral fragrances.

In addition, the mixtures of damascenone and 2,2,6-trimethyl-1-cyclohexen-1-ylacetaldehyde (or beta-cyclohomocitral) of our invention are capable of supplying and/or potentiating certain flavor and aroma notes usually lacking in many fruit flavors, wine flavors, and "fermented" type flavors as well as tobacco flavors heretofore provided. Furthermore, the mixtures of damascenone and beta-cyclohomocitral of our invention are capable of supplying certain fragrance notes usually lacking in many perfumery materials, for example, rose fragrances.

Contemplated within the scope of our invention are weight ratios of damascenone:beta-cyclohomocitral of from 1:99 up to 99:1. It is, however, preferable in the practice of our invention to use weight ratios of damascenone:beta-cyclohomocitral of from about 1:20 up to about 1:1. From an economical as well as an organoleptic standpoint, the most preferable weight ratio of damascenone:beta-cyclohomocitral is from about 1:20 up to about 1:10.

When the beta-cyclohomocitral or the mixtures of damascenone and beta-cyclohomocitral of our invention are used as food flavor adjuvants, the nature of the co-ingredients included with the said mixtures of damascenone and beta-cyclohomocitral in formulating the product composition will also serve to alter the organoleptic characteristics of the ultimate foodstuff treated therewith.

As used herein in regard to flavors, the terms "alter" and "modify" in their various forms means "supplying or imparting flavor character or note to otherwise bland, relatively tasteless substances or augmenting the existing flavor characteristic where a natural flavor or synthetic flavor or mixture of natural and synthetic flavors is deficient in some regard, or supplementing the existing flavor impression to modify its quality, character or taste."

As used herein, the term "enhance" is intended to mean the intensification (without effecting a change in kind of quality of aroma or taste) of one or more taste and/or aroma nuances present in the organoleptic impression of a consumable

material, e.g. foodstuff, tobacco, chewing gum, medicinal product, perfume composition or perfumed article.

As used herein the term "foodstuff" includes both solid and liquid ingestible materials which usually do, but need not, have nutritional value. Thus, foodstuffs include soups, convenience foods, beverages, dairy products, candies, vegetables, cereals, soft drinks snacks and the like.

As used herein the term "chewing gum" is intended to mean a composition which comprises a substantially water-insoluble, chewable plastic gum base such as chicle, or substitutes therefor, including jelutung, guttakay rubber and/or certain comestible natural or synthetic resins or waxes. Incorporated within the gum base, in admixture therewith may be plasticizers or softening agents, e.g. glycerine; and a flavoring composition which incorporates beta-cyclohomocitral or a mixture of damascenone and beta-cyclohomocitral of our invention, and, in addition, sweetening agents which may be sugars, including sucrose or dextrose and/or artificial sweeteners including dipeptides, cyclamates and saccharin. Other optional ingredients may also be present.

The term "medicinal product" includes both solids and liquids which are ingestible, non-toxic materials having medicinal value such as cough syrups, cough drops, toothpaste, aspirin and chewable medicinal tablets as further exemplified herein.

Substances suitable for use herein as co-ingredients or flavoring adjuvants are well known in the art for such use being extensively described in the relevant literature. Such material is required to be "ingestibly" acceptable and thus non-toxic or otherwise non-deleterious. Particularly critical is the additional requirement that such material be organoleptically compatible with beta-cyclohomocitral or mixtures of damascenone and beta-cyclohomocitral encompassed within the scope of our invention. Also critical is the additional requirement that such material be nonreactive (within the range of storage conditions and room temperature use conditions) with each of damascenone and beta-cyclohomocitral.

Accordingly, such materials which may in general be characterized as flavoring adjuvants or vehicles comprise broadly stabilizers, thickeners, surface active agents, conditioners, other flavorants and flavor intensifiers.

Stabilizer compounds include preservatives, e.g., sodium chloride; antioxidants, e.g. calcium and sodium ascorbate, ascorbic acid, butylated hydroxy-anisole (mixture of 2- and 3-tertiary-butyl-4-hydroxy-anisole), butylated hydroxy toluene, (2,6-di-tertiary-butyl-4-methyl phenol), propyl gallate and the like and sequestrants, e.g., citric acid.

Thickener compounds include carriers, binders, protective colloids, suspending agents, emulsifiers and the like, e.g., agaragar, carrageenan; cellulose and cellulose derivatives such as carboxymethyl cellulose and methyl cellulose; natural and synthetic gums such as gum arabic, gum tragacanth; gelatin, proteinaceous materials; lipids, carbohydrates, starches, pectins, and emulsifiers, e.g., mono- and diglycerides of fatty acids, skim milk powder, hexoses, pentoses, disaccharides, e.g., sucrose corn syrup and the like.

Surface active agents include emulsifying agents, e.g., fatty acids such as capric acid, caprylic acid, palmitic acid, myristic acid and the like, mono- and diglycerides of fatty acids, lecithin, defoaming and flavor-dispersing agents such as sorbitan monostearate, potassium stearate, hydrogenated tallow alcohol and the like.

Conditioners include compounds such as bleaching and maturing agents, e.g., benzoyl peroxide, calcium peroxide, hydrogen peroxide and the like; starch modifiers such as peracetic acid, sodium chlorite, sodium hypochlorite, propylene oxide, succinic anhydride and the like, buffers and neutralizing agents, e.g., sodium acetate, ammonium bicarbonate, ammonium phosphate, citric acid, lactic acid, vinegar and the like; colorants, e.g., carminic acid, cochineal, tumeric and curcuma and the like; firming agents such as aluminum sodium sulfate, calcium chloride and calcium gluconate; texturizers, anti-caking agents, e.g., aluminum calcium sulfate and tribasic calcium phosphate; enzymes, yeast foods, e.g., calcium lactate and calcium sulfate; nutrient supplements, e.g., iron salts such as ferric phosphate, ferrous gluconate and the like, riboflavin, vitamins, zinc sources such as zinc chloride, zinc sulfate and the like.

Other flavorants and flavor intensifiers include organic acids, e.g., acetic acid, formic acid, 2-hexenoic acid, benzoic acid, n-butyric acid, caproic acid, caprylic acid, cinnamic acid, isobutyric acid, isovaleric acid, alpha-methyl-butyric acid, propionic acid, valeric acid, 2-methyl-2-pentenoic acid, and 2-methyl-3-pentenoic

acid; ketones and aldehydes, e.g., acetaldehyde, acetophenone, acetone, acetyl methyl carbinol, acrolein, n-butanal, crotonal, diacetyl, beta, beta-dimethyl-acrolein, n-hexanal, 2-hexenal, cis-3-hexenal, 2-heptanal, 4-(p-hydroxyphenyl)-2-butanone, alpha-ionone, beta-ionone, methyl-3-butanone, 2-pentanone, 2-pentenal and propanal; alcohols such as 1-butanal, benzyl alcohol, 1-borneol, trans-2-buten-1-ol, ethanol, geraniol, 1-hexanal, 2-heptanol, trans-2-hexenol-1, cis-3-hexen-1-ol, 3-methyl-3-buten-1-ol, 1-pentenol, 1-penten-3-ol, p-hydroxyphenyl-2-ethanol, isoamyl alcohol, isofenchyl alcohol, phenyl-2-ethanol, alpha-terpineol, cis-terpineol hydrate, esters, such as butyl acetate, ethyl acetate, ethyl acetoacetate, ethyl benzoate, ethyl butyrate, ethyl caproate, ethyl cinnamate, ethyl crotonate, ethyl formate, ethyl isobutyrate, ethyl isovalerate, ethyl alpha-methylbutyrate, ethyl propionate, ethyl salicylate, trans-2-hexenyl acetate, hexyl acetate, 2-hexenyl butyrate, hexyl butyrate, isoamyl acetate, isopropyl butyrate, methyl acetate, methyl butyrate, methyl caproate, methyl isobutyrate, alpha-methylbutyrate, propyl acetate, amyl acetate, amyl butyrate, benzyl salicylate, dimethyl anthranilate, ethyl methylphenylglycidate, ethyl succinate, isobutyl cinnamate and terpenyl acetate; essential oils, such as jasmine absolute, rose absolute, orris absolute, lemon essential oil, Bulgarian rose, yara yara, natural raspberry oil and vanilla; lactones; sulfides, e.g., methyl sulfide and other materials such as maltol, acetoin and acetals (e.g., 1,1-diethoxyethane, 1,1-dimethoxyethane and dimethoxy-methane.

The specific flavoring adjuvant selected for use may be either solid or liquid depending upon the desired physical form of the ultimate product, i.e., foodstuff, whether simulated or natural, and should, in any event, be capable of providing an environment in which the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral can be dispersed or admixed to provide a homogeneous medium. In addition, selection of one or more flavoring adjuvants, as well as the quantities thereof will depend upon the precise organoleptic character desired in the finished product. Thus, in the case of flavoring compositions, ingredient selection will vary in accordance with the foodstuff in which the flavor and aroma are to be imparted. In contradistinction, in the preparation of solid products, e.g., simulated foodstuffs, ingredients capable of providing normally solid compositions should be selected such as various cellulose derivatives.

As will be appreciated by those skilled in the art, the amount of beta-cyclohomocitral or mixture of damascenone and beta-cyclohomocitral employed in a particular instance can vary over a relatively wide range whereby to its desired organoleptic effects having reference to the nature of the product are achieved. Thus, correspondingly, greater amounts would be necessary in those instances wherein the ultimate food composition to be flavored is relatively bland to the taste, whereas relatively minor quantities may suffice for purposes of enhancing the composition merely deficient in natural flavor or aroma. The primary requirement is that the amount selected be effective, i.e., sufficient to alter, modify or enhance the organoleptic characteristics of the parent composition, whether foodstuff per se or flavoring composition.

The use of insufficient quantities of beta-cyclohomocitral or mixture of damascenone and beta-cyclohomocitral will, of course, substantially vitiate any possibility of obtaining the desired results while excess quantities prove needlessly costly and in extreme cases, may disrupt the flavor-aroma balance, thus proving self-defeating. Accordingly, the terminology "effective amount" and "sufficient amount" is to be accorded a significance in the context of the present invention consistent with the obtention of desired flavoring effects.

Thus, and with respect to ultimate food compositions, it is found that quantities of beta-cyclohomocitral or mixture of damascenone and beta-cyclohomocitral ranging from a small but effective amount, e.g., 0.2 parts per million up to about 50 parts per million by weight based on total composition are suitable. Concentrations in excess of the maximum quantity stated are not normally recommended, since they fail to prove commensurate enhancement of organoleptic properties. In those instances, wherein the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral is added to the foodstuff as an integral component of a flavoring composition, it is, of course, essential that the total quantity of flavoring composition employed be sufficient to yield an effective concentration (of beta-cyclohomocitral or mixture of damascenone and beta-cyclohomocitral) in the foodstuff product.

Food flavoring compositions prepared in accordance with the present invention preferably contain the beta-cyclohomocitral or the mixture of

damascenone and beta-cyclohomocitral in concentrations ranging from about 0.1% up to about 15% by weight based on the total weight of the said flavoring composition.

The compositions described herein can be prepared according to conventional techniques well known as typified by cake batters and fruit drinks and can be formulated by merely admixing the involved ingredients within the proportions stated in a suitable blender to obtain the desired consistency, homogeneity of dispersion, etc. Alternatively, flavoring compositions in the form of particulate solids can be conveniently prepared by mixing the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral with, for example, gum arabic, gum tragacanth, carrageenan and the like, and thereafter spray-drying the resultant mixture thereby to obtain the particulate solid product. Pre-prepared flavor mixes in powder form, e.g., a fruit-flavored powder mix are obtained by mixing the dried solid components, e.g., starch, sugar and the like and the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral in a dry blender until the requisite degree of uniformity is achieved.

It is presently preferred to combine with the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral; the following adjuvants: p-Hydroxybenzyl acetone; Geraniol; Acetaldehyde; Maltol; Ethyl methyl phenyl glycidate; Benzyl acetate; Dimethyl sulfide; Vanillin; Methyl cinnamate; Ethyl pelargonate; Methyl anthranilate; Isoamyl acetate; Isobutyl acetate; Alpha ionone; Ethyl butyrate; Acetic acid; Gamma-undecalactone; Naphthyl ethyl ether; Diacetyl; Ethyl acetate; Anethole; Isoamyl butyrate; Cis-3-hexenol-1; 2-Methyl-2-pentenoic acid; Elemecine (4-allyl-1,2,6-trimethoxy benzene); Isoelemecine (4-propenyl-1,2,6-trimethoxy benzene); and 2-(4-hydroxy-4-methylpentyl) norbornadiene.

An additional aspect of our invention provides an organoleptically improved smoking tobacco product and additives therefor, as well as methods of making the same which overcome specific problems heretofore encountered in which specific desired woody flavor characteristics of natural tobacco are created or enhanced and may be readily controlled and maintained at the desired uniform level regardless of variations in the tobacco components of the blend.

This invention further provides improved tobacco additives and methods whereby various desirable woody flavoring characteristics with sweet, floral, fruity, earthy and green notes may be imparted to smoking tobacco products and may be readily varied and controlled to produce the desired uniform flavoring characteristics.

In carrying out this aspect of our invention, we add to smoking tobacco materials or a suitable substitute therefor (e.g., dried lettuce leaves) an aroma and flavor additive containing as an active ingredient either (i) beta-cyclohomocitral, or (ii) a mixture of damascenone and beta-cyclohomocitral.

In addition to the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral of our invention, other flavoring and aroma additives may be added to the smoking tobacco material or substitute therefor either separately or in admixture with the beta-cyclohomocitral or the beta-cyclohomocitral-damascenone mixture as follows:

I. *Synthetic Materials*: Beta-ethyl-cinnamaldehyde; Eugenol; Dipentene; Damascenone; Maltol; Ethyl maltol; Delta undecalactone; Delta decalactone; Benzaldehyde; Amyl acetate; Ethyl butyrate; Ethyl valerate; Ethyl acetate; 2-Hexenol-1,2-methyl-5-isopropyl-1,3-nonadiene-8-one; 2,6-Dimethyl-2,6-undecadiene-10-one; 2-Methyl-5-isopropyl acetophenone; 2-Hydroxy-2,5,5,8a-tetramethyl-1-(2-hydroxyethyl)-decahydronaphthalene; Dodecahydro-3 $\alpha$ ,6,6,9a-tetramethyl naphthol-(2,1-b)-furan; 4-Hydroxy hexanoic acid, gamma lactone; Polyisoprenoid hydrocarbons defined in Example V of U.S. Patent 3,589,372 issued on June 29, 1971.

II. *Natural Oils*: Celery seed oil; Coffee extract; Bergamot oil; Cocoa extract; Nutmeg oil; Origanum oil.

An aroma and flavoring concentrate containing the beta-cyclohomocitral or a mixture of damascenone and beta-cyclohomocitral and, if desired, one or more of the above-indicated additional flavoring additives may be added to the smoking tobacco material, to the filter or to the leaf or paper wrapper. The smoking tobacco material may be shredded, cured, cased and blended tobacco material or reconstituted tobacco material or tobacco substitutes (e.g., lettuce leaves) or mixtures thereof. The proportions of flavoring additives may be varied in accordance with taste but insofar as enhancement or the imparting of natural and/or sweet notes, we

have found that satisfactory results are obtained if the proportion by weight of the sum total of beta-cyclohomocitral or mixture of damascenone and beta-cyclohomocitral to smoking tobacco material is between 125 ppm and 1,500 ppm (0.125%—0.15%) of the active ingredients to the smoking tobacco material. We have further found that satisfactory results are obtained if the proportion by weight of the sum total of beta-cyclohomocitral or mixture of damascenone and beta-cyclohomocitral used to flavoring material is between 1,000 and 10,000 ppm (0.10%—1.5%).

Any convenient method for incorporating the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral in the tobacco product may be employed. Thus, the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral taken alone or along with other flavoring additives may be dissolved in a suitable solvent such as ethanol, pentane, diethyl ether and/or other volatile organic solvents and the resulting solution may either be spread on the cured, cased and blended tobacco material or the tobacco material may be dipped into such solution. Under certain circumstances, a solution of the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral taken alone or taken further together with other flavoring additives as set forth above, may be applied by means of a suitable applicator such as a brush or roller on the paper or leaf wrapper for the smoking product, or it may be applied to the filter by either spraying, or dipping or coating.

Furthermore, it will be apparent that only a portion of the tobacco or substitute therefor need be treated and the thus-treated tobacco may be blended with other tobaccos before the ultimate tobacco product is formed. In such cases, the tobacco treated may have the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral in excess of the amounts or concentrations above indicated so that when blended with other tobaccos, the final product will have the percentage within the indicated range.

In accordance with one specific example of our invention, an aged, cured and shredded domestic burley tobacco is spread with a 10% ethyl alcohol solution of 1:1 mixture of damascenone and beta-cyclohomocitral in an amount to provide a tobacco composition containing 400 ppm by weight of beta-cyclohomocitral-damascenone mixture on a dry basis. Thereafter, the alcohol is removed by evaporation and the tobacco is manufactured into cigarettes by the usual techniques. The cigarette when treated as indicated has a desired and pleasing aroma which is detectable in the main and side streams when the cigarette is smoked. This aroma is described as being sweeter, rich, less harsh, more tobacco-like and having excellent woody, "cigar-box" like notes.

In accordance with another specific example of our invention an aged, cured and shredded domestic burley tobacco is spread with a 20% ethyl alcohol solution of beta-cyclohomocitral in an amount to provide a tobacco composition containing 800 ppm by weight of beta-cyclohomocitral on a dry basis. Thereafter, the alcohol is removed by evaporation and the tobacco is manufactured into cigarettes by the usual techniques. The cigarette when treated as indicated has a desired and pleasing aroma which is detectable in the main and side streams when the cigarette is smoked. This aroma is described as being sweeter, rich, less harsh, more tobacco-like and having woody, damascenone-like notes.

While our invention is particularly useful in the manufacture of smoking tobacco, such as cigarette tobacco, cigar tobacco and pipe tobacco, other tobacco products formed from sheeted tobacco dust or fines may also be used. Likewise, the beta-cyclohomocitral or the mixture of damascenone and beta-cyclohomocitral of our invention can be incorporated with materials such as filter tip materials, seam paste, packaging materials, and the like which are used along with tobacco to form a product adapted for smoking. Furthermore, the beta-cyclohomocitral, or the beta-cyclohomocitral-damascenone mixture can be added to certain tobacco substitutes of natural or synthetic origin (e.g., dried lettuce leaves) and, accordingly, by the term "tobacco" as used throughout this specification is meant any composition intended for human consumption by smoking or otherwise, whether composed of tobacco plant parts or substitute materials or both.

The beta-cyclohomocitral and one or more auxiliary perfume ingredients, including, for example, alcohols, aldehydes, nitriles, esters, cyclic esters, and natural essential oils, may be admixed so that the combined odors of the individual components produce a pleasant and desired fragrance, particularly and preferably in floral fragrances, rosey fragrances, muguet fragrances or petitgrain fragrances. Such perfume compositions usually contain (a) the main note or "bouquet" or



foundation stone of the composition; (b) modifiers which round off and accompany the main note; (c) fixatives which include odorous substances which lend a particular note to the perfume throughout all stages of evaporation and substances which retard evaporation; and (d) topnotes which are usually low boiling fresh smelling materials.

In perfume compositions, the individual components which contribute its particular olfactory characteristics, but the over-all effect of the perfume composition will be the sum of the effects of each of the ingredients. Thus, the beta-cyclohomocitral can be used to alter the aroma characteristics of a perfume composition, for example, by utilizing or moderating the olfactory reaction contributed by another ingredient in the composition.

The amount of beta-cyclohomocitral of our invention which will be effective in perfume compositions depends on many factors, including the other ingredients, their amounts and the effects which are desired. It has been found that perfume compositions containing as little as 0.1% beta-cyclohomocitral or less (e.g., 0.05%) can be used to impart earthy, woody, green, floral and rose notes to soaps, cosmetics and other products. In addition, it has been found that such perfume compositions containing as little as 0.05% of beta-cyclohomocitral can be used to alter, modify or enhance earthy, woody, green, floral and rose notes already present in soaps, cosmetics and other products. The amount employed can range up to 10% of the fragrance components and will depend on considerations of cost, nature of end product, the effect desired on the finished product and the particular fragrance sought.

The beta-cyclohomocitral is useful, taken alone or in perfume compositions as an olfactory component in detergents and soaps, space odorants and deodorants, perfumes, colognes, toilet water, bath preparations, such as bath oils and bath solids; hair preparations such as lacquers, brilliantines, pomades and shampoos; cosmetic preparations such as creams, deodorants, hand lotions and sun screens, powders such as talcs, dusting powders, face powders and the like. As little as 1% of beta-cyclohomocitral will suffice to impart a green, earthy note to petitgrain formulations. As little as 4% of beta-cyclohomocitral will suffice to impart or enhance a rosey note in floral or muguet formulations. Generally, no more than 10% of beta-cyclohomocitral based on the ultimate end product is required in the perfume composition.

Furthermore, the mixture of damascol (phenyl  $C_6$  ketone) and beta-cyclohomocitral of our invention and one or more auxiliary perfume ingredients, including, for example, alcohols, aldehydes, nitriles, esters, cyclic esters, and natural essential oils, may be admixed so that the combined odors of the individual components produce a pleasant and desired fragrance, particularly and preferably in rose, muguet and other "floral" fragrances. It is to be understood that such additional adjuvants are to be organoleptically compatible with both of said phenyl  $C_6$  ketone and beta-cyclohomocitral, and, further, that such adjuvants are to be non-reactive under use conditions at room temperature and storage conditions with said phenyl  $C_6$  ketone and said beta-cyclohomocitral.

The mixture of the damascol and beta-cyclohomocitral can be used to alter the aroma characteristics of a perfume composition (or enhance same) for example, by utilizing or moderating the olfactory reaction contributed by another ingredient in the composition.

As is the case when using the beta-cyclohomocitral alone (without a damascol or damascenone), the amount of mixture of the damascol and beta-cyclohomocitral of our invention which will be effective in perfume compositions depends on many factors, including the other ingredients, their amounts and the effects which are desired. It has been found that perfume compositions containing as little as 0.01% of mixture of damascol and beta-cyclohomocitral and even less (e.g., 0.005%) can be used to impart a rosey or muguet aroma to cosmetics or other products. The amount employed can range up to 10% of the fragrance components and will depend on considerations of cost, nature of the end product, the effect desired on the finished product and the particular fragrance sought.

The mixture of the damascol and beta-cyclohomocitral is useful, taken alone or in perfume compositions as an olfactory component in detergents and soaps, space odorants and deodorants, perfumes, colognes, toilet water, bath preparations, such as bath oils, and bath solids; hair preparations, such as lacquers, brilliantines, pomades and shampoos; cosmetic preparations, such as creams, deodorants, hand lotions and sun screens; powders, such as talcs, dusting powders, face powders and the like. When used as an olfactory component as little as 1% of the damascol-beta-

cyclohomocitral mixture will suffice to impart a green, earthy note to petitgrain formulations. Generally, no more than 3% of the damascol-beta-cyclohomocitral mixture based on the ultimate end product is required in the perfume composition.

5 Contemplated within the scope of our invention are weight ratios of damascol (or phenyl  $C_6$  ketone):beta-cyclohomocitral of 1:1 up to 5:1. It is, however, preferably in the practice of our invention to use weight ratios of damascol:beta-cyclohomocitral of from about 2:1 up to about 4:1. 5

10 In addition, the mixture of damascenone and beta-cyclohomocitral and one or more auxiliary perfume ingredients, including, for example, alcohols, aldehydes, nitriles, esters, cyclic esters, and natural essential oils, may be admixed so that the combined odors of the individual components produce a pleasant and desired fragrance, particularly and preferably in rose and other "floral" fragrances. 10

15 As is the case when using beta-cyclohomocitral without a damascol or damascenone, the amount of mixture of damascenone and beta-cyclohomocitral of our invention which will be effective in perfume compositions depends on many factors, including the other ingredients, their amounts and the effects which are desired. It has been found that perfume compositions containing as little as 0.01% of mixture of damascenone and beta-cyclohomocitral and even less (e.g., 0.005%) can be used to impart a rosey aroma with earthy and green notes to soaps, 20 cosmetics or other products. The amount employed can range up to 10% of the fragrance components and will depend on considerations of cost, nature of the end product, the effect desired and the finished product and the particular fragrance sought. 20

25 The mixture of damascenone and beta-cyclohomocitral is useful, taken alone or in perfume compositions as an olfactory component in detergents and soaps, space odorants, and deodorants, perfumes, colognes, toilet water, bath preparations, such as bath oils, and bath solids; hair preparations, such as lacquers, brilliantines, pomades and shampoos; cosmetic preparations, such as creams, deodorants, hand lotions and sun screens; powders, such as talcs, dusting powders, 30 face powders and the like. When used as an olfactory component as little as 1% of the damascenone-beta-cyclohomocitral mixture of our invention will suffice to impart an intense rosey fragrance to muguet formulations. Generally, no more than 3% of the damascenone-beta-cyclohomocitral mixture based on the ultimate end product is required in the perfume composition. 30

35 In addition, the perfume composition or fragrance composition of our invention can contain a vehicle, or carrier food for either (i) beta-cyclohomocitral taken alone; or (ii) the phenyl  $C_6$  ketone-beta-cyclohomocitral mixture, or (iii) the damascenone-beta-cyclohomocitral mixture. The vehicle can be liquid such as an alcohol, a non-toxic alcohol, a non-toxic glycol, or the like. The carrier can also be an absorbent solid, such as a gum (e.g., gum arabic) or components for encapsulating the composition (such as gelatin). 40

45 It will thus be apparent that the beta-cyclohomocitral or the damascenone-beta-cyclohomocitral mixture or the beta-cyclohomocitral-phenyl  $C_6$  ketone mixture of our invention can be utilized to alter the sensory properties, particularly organoleptic properties, such as flavor and/or fragrance of a wide variety of consumable materials. 45

50 Examples I, II, IV—VIII, X, XIV, XVI, XXIII and XXIV, following, serve to illustrate processes for producing beta-cyclohomocitral useful in our invention. Example IX, following, serves to illustrate the unworkability of this process where dimethyl formamide is used in the oxidation reaction of beta-ionone with peracetic acid. Example III, serves to illustrate the unworkability of the reaction where no buffer, e.g., sodium acetate, is used. Example XV illustrates the unworkability of the above process in forming alpha-ionone enol ester when operated on alpha-ionone rather than beta-ionone. Examples XI—XIII, XVII—XXII and 55 XXV—XXXV illustrate the utility of beta-cyclohomocitral per se. 55

Examples XXXVI—LII illustrate the utility of the damascenone-beta-cyclohomocitral mixtures of our invention.

Examples LIII—LXIII illustrate the utility of the damascol-beta-cyclohomocitral mixtures of our invention.

60 It will be understood that these Examples are illustrative and the invention is to be considered restricted thereto only as indicated in the appended claims. All parts and percentages given herein are by weight unless otherwise specified. 60

## EXAMPLE 1.

## A. PRODUCTION OF BETA-IONONE ENOL ESTER FROM BETA-IONONE

Into a two liter reaction flask equipped with stirrer, thermometer, reflux condenser, addition funnel and cooling bath, the following materials are added:

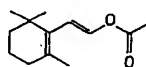
- (i) Solution of 96 grams beta-ionone in 300 cc chloroform;  
(ii) 30 grams sodium acetate

95 Grams and 40 percent peracetic acid is then added with cooling, slowly at 10°C during a period of one hour. The reaction mass is stirred at 10°C for an additional hour and the solution is then allowed to slowly warm up to room temperature. The reaction mass is then poured into one liter of water and the resultant organic and aqueous phases are separated. The aqueous phase is then extracted with 100 cc of chloroform and the resultant organic phases are then bulked. The solvent is evaporated from the organic phase to yield 99.5 grams of an oil which is then chromatographed on 1,000 grams of alumina deactivated with 5% w/w water and eluted as follows:

Fraction	Volume of Solvent	Quantity of Solute Eluted
1	750 cc hexane	8.0 grams
2	500 cc hexane	31.7 grams
3	300 cc hexane	13.5 grams
4	250 cc hexane	7.0 grams
5	250 cc hexane	1.9 grams
6	250 cc hexane	1.6 grams
7	600 cc 25% diethyl ether-75% hexane	15.6 grams
8	600 cc diethyl ether	15.3 grams

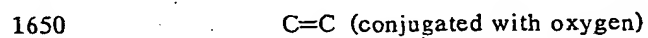
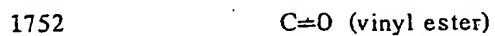
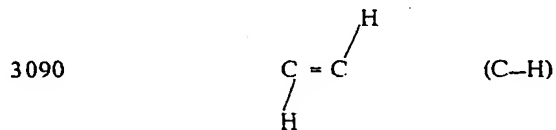
Fractions 1—4 are composed mainly of beta-ionone enol ester.

The spectral data for a purified sample of this material obtained by preparative gas chromatography confirm the structure:



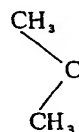
The mass spectrum of this compound has the following fragmentation pattern, in decreasing order of ion abundance:

m/e 166 (100), 151 (81), 43 (30), 208 (30) (molecular ion) and 90 (18). The infrared spectrum shows the following characteristic absorption bands (cm<sup>-1</sup>):



1360

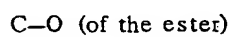
1380



1365

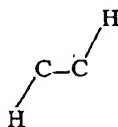


1215



1080

930



5

5

10

NMR spectrum exhibits in CDCl<sub>3</sub> solution the following proton absorptions (chemical shifts in ppm):

10

Ppm	Multiplicity	Assignment	No. of Protons
1.00	(s)	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} \end{array}$	6H
1.70-1.40	(m)	$\left. \begin{array}{l} -\text{CH}_2- \\ =\text{C}-\text{CH}_3 \end{array} \right\}$	7H
1.76	(s)		
2.00	(t)	=C-CH <sub>2</sub> -	2H
2.16	(s)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} \\ \mid \\ \text{O} \end{array}$	3H
5.86 and 7.20	(m)	Olefinic protons	2H

15

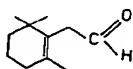
15

# HYDROLYSIS TO FORM BETA-CYCLOHOMOCITRAL FROM BETA-IONONE ENOL ESTER

Beta-ionone enol ester (60.2 grams from Fractions 1—4 produced in Part A) is added to 280 cc of 10 percent potassium hydroxide solution (in a 50:50 water:methanol mixture at room temperature and stirred for a period of 30 minutes. Water 1,000 cc is added to the reaction mass which is then extracted with three 250 cc portions of diethyl ether. The combined ether extract is washed twice with two 100 cc portions of saturated sodium chloride solution, dried over anhydrous magnesium sulfate and evaporated to obtain 53 grams of an oil, beta-cyclohomocitral.

The crude beta-cyclohomocitral is distilled at 2 mm Hg pressure and the fraction boiling at 70—80°C is collected (35.6 g).

Gas chromatographic analysis indicates that the product is about 85% pure. A pure sample of beta-cyclohomocitral is obtained by preparative chromatography (conditions: 10' x 1/4" 10% carbowax 20M- packed stainless steel column at 220°C isothermal) and is characterised by the following analytical data as:



The word "Carbowax" is a Trade Mark.

Mass spectral fragmentation, in decreasing order of ion abundance:  
m/e (%) 107(100); 29(93); 151(90); 41(88); 81(80); 95(67); 123(57); 55(45); 39(45); 27(43); 166(Mol ion) (35).

The infrared spectrum shows the following characteristic absorption bands (cm<sup>-1</sup>):

2760	$\begin{array}{c} \text{O} \\    \\ \text{C} - \text{H} \end{array}$
1770	C = O (unconjugated)
1380, 1360	$\begin{array}{cc} \text{CH}_3 & \text{CH}_3 \\ & \diagdown \quad \diagup \\ & \text{C} \end{array}$
1375	-CH <sub>3</sub>

The NMR spectrum of the compound is in agreement with the above structure:

	(PPM)	Multiplicity	Assignment	No. of Protons	
	0.98	(s)	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C} \\   \\ \text{CH}_3 \end{array}$	6H	
	1.58	(s)	-C-CH <sub>3</sub>	9H	
	1.80 - 1.42	(m)	-CH <sub>2</sub> -		
5	2.00	(t)	$\begin{array}{c} \text{O} \\    \\ \text{-C-CH}_2\text{-C} \end{array}$	2H	5
	9.58	(t)	HC-O	1H	

## EXAMPLES II—X.

10 The following examples, carried out using the same procedure as Example I, illustrate the results which occur when parameters of the oxidation reaction of beta-ionone with peracetic acid are varied, e.g., as to buffer, solvent, temperature, presence of organic base and ratio of organic alkanolic acid to peracetic acid. The percentages given are obtained by gas chromatographic analyses of the reaction mixture after 30 minutes and do not represent yields of isolated material. 10

15	Example No.	% Enol Ester	% Starting Material	% By-Products	Reactants and Reaction Conditions	15
20	II	47	24	29	Acetic acid—(150 cc) Sodium acetate (20 g) Beta-ionone—(30 g) 40% peracetic acid—(30 g) Temperature: 23°C.	20
25	III	12	52	36	Acetic acid—(150 g) Beta-ionone—(30 g) 40% peracetic acid—(30 g) Temperature: 25°C.	25
30	IV	40	29	31	Cyclohexane (150 cc) Sodium acetate (20 g) Beta-ionone (30 g) 40% peracetic acid (30 g) Temperature: 25°C.	30
35						35

	Example No.	% Enol Ester	% Starting Material	% By-Products	Reactants and Reaction Conditions	
5	V	52	26	22	Acetic acid (150 cc) Potassium acetate (35 g) Beta-ionone (30 g) 40% peracetic acid (30 g) Temperature: 25°C.	5
10						10
15	VI	31	30	39	Formic acid (150 cc) Potassium acetate (50 g) Beta-ionone (30 g) 40% peracetic acid (30 g) Temperature: 25°C.	15
20						20
25	VII	49	6	45	Acetic acid (150 cc) Potassium acetate (35 g) Beta-ionone (30 g) 40% peracetic acid (33 g) Temperature: 25°C.	25
30	VIII	36	21	43	Acetic acid (150 cc) Potassium acetate (35 g) Beta-ionone (30 g) 40% Peracetic acid (33 g) Temperature: 50°C.	30
35						35
40	IX	0	9	91 Beta-ionone epoxide	Dimethyl formamide (150 cc) Beta-ionone (30 g) 40% peracetic acid (33 g) Temperature: 4 days at a temperature of 18°C.	40
45						45
50	X	55	17	28	Acetic acid (450 cc) Potassium acetate (105 g) Beta-ionone (96 g) 40% peracetic acid (105 g) Temperature: 25°C.	50
55						55

## EXAMPLE XI.

## PETITGRAIN FORMULATION

The following mixture is prepared:

	Ingredients	Parts by Weight	
5	Betacyclohomocitral prepared according to the process of Example I	20	5
	Linalool	500	
	Linalyl Acetate	600	
10	Dimethyl Anthranilate	2	10
	Terpineol	20	
	Geraniol	30	
	Terpinyl Acetate	10	
	Geranyl Acetate	5	
15	Ocimene	20	15
	Limonene	50	
	Pinene	20	
	Nerolidol	10	

20 The beta-cyclohomocitral imparts the green, earthy note of petitgrain required in such petitgrain formulations. 20

## EXAMPLE XII.

## PREPARATION OF A SOAP COMPOSITION

25 100 grams of soap chips are mixed with one gram of the perfume composition of Example XI until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent petitgrain character with excellent green earthy notes. 25

## EXAMPLE XIII.

## PREPARATION OF A DETERGENT COMPOSITION

30 A total of 100 grams of detergent powder is mixed with 0.15 grams of the perfume composition of Example XI, until a substantially homogeneous composition is obtained. This composition has an excellent petitgrain aroma with earthy green notes. 30

## EXAMPLE XIV.

PREPARATION OF BETA-CYCLOHOMOCITRAL BY H<sub>2</sub>O<sub>2</sub> PEROXIDATION OF BETA-IONONE

35 To 20 grams of beta-ionone in 100 ml methanol is added 12 ml of 30% hydrogen peroxide. The solution is then cooled to 15°C and 18 ml 6 molar aqueous sodium hydroxide is added over a period of 30 minutes while maintaining the reaction mixture at 15°C. The reaction mixture is then allowed to warm up to 30°C and then maintained at 30°C with external cooling. The exotherm lasts approximately 60 minutes. Examination of the reaction product by gas chromatography indicates that some beta-ionone is still present. An additional 12 ml of 30% H<sub>2</sub>O<sub>2</sub> and 18 ml 6 molar aqueous NaOH are added during a 30-minute period while maintaining the temperature at 25°C. Again an exotherm occurs lasting approx- 40

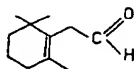


imately 60 minutes during which time the temperature is maintained at 30°C. The reaction mass is then poured into excess water (500 ml) and the product is then extracted with three 150 ml portions of diethyl ether. The combined ether extracts are then washed with two 150 ml portions of saturated sodium chloride solution and dried over anhydrous MgSO<sub>4</sub>. The solvent is then evaporated to yield 16.8 grams of a crude oil.

Examination of this material by gas chromatography indicates 22% beta-cyclohomocitral.

The desired product is obtained by preparative gas chromatography (conditions: 10' x 1/4" 10% Carbowax 20 M packed stainless steel column at 220°C isothermal).

The structure is confirmed by IR, MS and NMR analyses as being:



#### EXAMPLE XV.

#### FORMATION OF ALPHA-IONONE EPOXIDE FROM ALPHA-IONONE

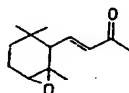
Into a 500 ml flask equipped with thermometer, stirrer, addition funnel and reflux condenser, the following materials are placed in the following order:

Ingredients	Amount
Acetic Acid	150 cc
Potassium Acetate	35 grams
Alpha-Ionone	30 grams

33 grams of 40% peracetic acid is then added dropwise into the reaction mass with stirring at 25°C over a 45-minute period. The reaction mass exotherms for approximately one hour and is then allowed to remain at room temperature for a period of 15 hours.

The reaction mass is then poured into 500 ml water and the product is extracted with three 150 cc portions of diethyl ether. The ether extracts are combined and washed with two 100 cc portions of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The residual oil obtained after stripping the solvent, is distilled at 93—99°C at 0.5 mm Hg pressure yielding 28.3 g of a clean colorless liquid.

IR, MS and NMR analyses confirm the fact that the product is alpha-ionone epoxide having the structure:



#### EXAMPLE XVI.

#### PRODUCTION OF BETA-CYCLOHOMOCITRAL

Into a two liter reaction flask equipped with stirrer, thermometer, addition funnel and cooling bath, the following materials are placed in the following order:

Ingredients	Amounts
Acetic Acid	450 cc
Potassium Acetate	150 g
Beta-Ionone	96 g

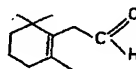
105 grams of 40% peracetic acid is then added dropwise to the reaction mass with cooling while maintaining the reaction mass at 25°C ± 2°C over a two-hour

period. The reaction mass is then stirred for an additional three-hour period (during the first hour a slight exotherm occurs) at 25°C.

The reaction mass is then poured into 1,000 ml water and the resultant product is extracted with three 300 cc volumes of diethyl ether. The ether extracts are combined and washed with two 150 cc portions of saturated sodium chloride solution. The resultant washed ether extract is then evaporated whereby 118 grams of residual oil is obtained.

400 cc of 10% potassium hydroxide solution (50:50 mixture, water:methanol) is prepared and the 118 grams of residual oil obtained above is added thereto. The resultant solution warms up slightly and is stirred for a period of 45 minutes.

The solution is then poured into 500 ml water and the product is extracted with three 250 cc portions of diethyl ether. The diethyl ether extract is then washed with two 200 cc portions of saturated sodium chloride solution, dried over anhydrous magnesium sulfate and evaporated to obtain 89 grams of a crude oil. This crude oil is distilled through a vigreux distillation column at 70–75°C and 2.0 mm Hg pressure to obtain 40.2 grams of a compound having the structure:



as confirmed by infrared (IR), nuclear magnetic resonance (NMR) and mass (MS) spectra.

#### EXAMPLE XVII.

##### PREPARATION OF A COSMETIC-POWDER COMPOSITION

A cosmetic powder is prepared by mixing in a ball mill, 100 g of talcum powder with 0.25 g of beta-cyclohomocitral prepared according to Example XVI. It has an excellent woody, earthy aroma with a rosey nuance.

#### EXAMPLE XVIII.

##### PERFUMED LIQUID DETERGENT

Concentrated liquid detergents with a woody, green, earthy odor are prepared containing 0.10%, 0.15% and 0.20% of beta-cyclohomocitral prepared according to Example XVI. They are prepared by adding and homogeneously mixing the appropriate quantity of beta-cyclohomocitral in the liquid detergent. The detergents all possess a woody, green, earthy fragrance with rosey nuances, the intensity increasing with greater concentrations of beta-cyclohomocitral.

#### EXAMPLE XIX.

##### PREPARATION OF A COLOGNE AND HANDKERCHIEF PERFUME

Beta-cyclohomocitral prepared according to the process of Example XVI is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). A distinct and definite woody, green, earthy fragrance with a rosey nuance is imparted to the cologne and to the handkerchief perfume.

#### EXAMPLE XX.

##### PREPARATION OF A COLOGNE AND HANDKERCHIEF PERFUME

The composition of Example XI is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). The use of the beta-cyclohomocitral in the composition of Example XI affords a distinct and definite strong petitgrain aroma with earthy and green notes to the handkerchief perfume and cologne.

#### EXAMPLE XXI.

##### PREPARATION OF A SOAP COMPOSITION

One hundred grams of soap chips are mixed with one gram of beta-cyclohomocitral until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent woody, green and earthy aroma with a rosey nuance.

## EXAMPLE XXII.

## PREPARATION OF A DETERGENT COMPOSITION

A total of 100 g of a detergent powder is mixed with 0.15 g of the beta-cyclohomocitral of Example XVI until a substantially homogeneous composition is obtained. This composition has an excellent woody, green, earthy aroma with a rosey nuance.

## EXAMPLE XXIII.

Perpropionic acid is prepared in the following manner. A mixture of the following materials:

160 ml propionic acid	} Referred to hereinafter as "Mixture A"
1 ml sulfuric acid (concentrated)	
40 g 50% hydrogen peroxide	

is allowed to stand for 20 hours at room temperature.

The following reactants are placed in a 500 ml reaction flask equipped with a stirrer and cooling bath:

140 ml propionic acid	} Referred to hereinafter as "Mixture B"
75 g potassium acetate	
60 g beta-ionone	

To the stirred Mixture B is added, dropwise, Mixture A over a 60-minute period while maintaining the reaction temperature at  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$  by means of external cooling. When the addition is complete the reaction mixture is stirred for an additional 2 hours at  $25^{\circ}\text{C}$ .

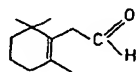
The reaction mixture is then poured into 1,000 ml water and extracted twice with 250 ml portions of diethyl ether. The combined ether extracts are then washed first with water (three 100 ml portions) and then with a saturated solution of sodium chloride (150 ml). The ether solution is then dried over anhydrous magnesium sulfate and the solvent evaporated to yield 78 g of crude oil containing propionic acid as well as product. The crude product is hydrolyzed with a solution of 40 g potassium carbonate in 300 ml of water by heating under reflux, with stirring, for 15 hours. After cooling the organic layer is collected and the aqueous layer is extracted with 200 ml of diethyl ether. After combining the organic materials the solvent is removed by evaporation to yield 57.5 g of oil which is distilled to yield 19.5 g of beta-cyclohomocitral (Yield: 37%).

## EXAMPLE XXIV.

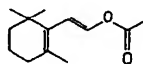
Performic acid is prepared in the following manner: 20 g 50% hydrogen peroxide and 80 ml of formic acid is admixed and the reaction mass is left at room temperature for 1.5 hours.

To a mixture consisting of 50 g of potassium acetate, 70 ml of acetic acid and 30 g of beta-ionone is added the preformed performic acid, prepared as described above, dropwise over a 30 minute period while maintaining the temperature of the stirred reaction mass at  $25^{\circ}\text{C}$  by means of external cooling. After the addition is complete, the mixture is stirred for a further 90 minutes at  $25^{\circ}\text{C}$  and is then poured into 800 ml of water. The product is extracted with two 200 ml portions of diethyl ether. The ether extracts are combined, washed with two 150 ml portions of saturated sodium chloride solution and then dried. Removal of the solvent by evaporation yields 32.5 g crude oil.

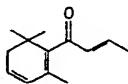
A gas chromatographic analysis of this material shows the following compositions:



(4%);



(41%);



(32%);

Other products 23%

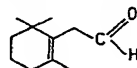
The following mixture is prepared:

29 g Lithium carbonate  
200 ml 50% aqueous methanol

To this is added the crude enol ester product obtained as described above. The mixture is then heated at 65—70°C until substantially complete hydrolysis of the enol ester to beta-cyclohomocitral as indicated by gas chromatographic analysis. Water is added to the reaction mass which is then extracted with three 100 cc portions of diethyl ether. The combined ether extracts are washed twice with two 100 cc portions of saturated sodium chloride solution, dried over anhydrous magnesium sulfate and evaporated to obtain an oil, beta-cyclohomocitral.

The crude is distilled at 2 mm Hg pressure and the fraction boiling at 70—80°C is collected.

Gas chromatographic analysis indicates that the product is about 85% pure. A pure sample of beta-cyclohomocitral is obtained by preparative chromatography and is characterised by the following analytical data as:



Mass spectral fragmentation, in decreasing order of ion abundance:  
m/e (%) 107(100); 29(93); 151(90); 41(88); 81(80); 95(67); 123(57); 55(45); 39(45); 27(43); 166(Mol ion) (35).

Infrared spectrum shows characteristic absorption

2760 cm <sup>-1</sup>	$\begin{array}{c} \text{O} \\    \\ \text{C} - \text{H} \end{array}$
1770 cm <sup>-1</sup>	C = O (unconjugated)
1380, 1360 cm <sup>-1</sup>	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} \end{array}$
1375 cm <sup>-1</sup>	-CH <sub>3</sub>

25

The NMR spectrum of the compound is in agreement with the above structure:

25

(PPM)	Multiplicity	Assignment	No. of Protons
0.98	(s)	$\begin{array}{c} \text{CH}_3 \\   \\ \text{C} \\   \\ \text{CH}_3 \end{array}$	6H
1.58	(s)	$\left. \begin{array}{l} =\text{CH}-\text{CH}_3 \\ -\text{CH}_2- \end{array} \right\}$	9H
1.80—1.42	(m)		
2.00	(t)	$\begin{array}{c} \text{O} \\    \\ =\text{C}-\text{CH}_2-\text{C} \end{array}$	2H
9.58	(t)	HC = O	1H

30

30

## EXAMPLE XXV.

## MUGUET PERFUME FORMULATION

The following formulation is prepared:

	Ingredient	Parts by Weight	
5	Indole	2	5
	Hexyl Cinnamic Aldehyde	400	
	Rhodinol	40	
	Terpineol	30	
	Tetrahydro-3-pentyl-pyran-4-ylacetate	10	
10	Cinnamyl Acetate	5	10
	4(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde	20	
	Hydroxy Citronellal	280	
15	Violet Leaves Absolute (10% in diethyl phthalate)	4	15
	Phenyl ethyl alcohol	45	
	Tetrahydromuguol	20	
	n-Undecylenic Aldehyde (10% in diethyl phthalate)	5	
20	n-decanal (10% in diethyl phthalate)	5	20
	n-nonanal (10% in diethyl phthalate)	4	
	Benzyl acetate	10	
	Dimethyl Phenyl Ethyl Carbinol	10	
25	p-t-butyl-alpha-methyl-hydrocinnamic aldehyde	4	25
	Methyl Cinnamate (10% in diethyl phthalate)	2	
	Benzyl Cinnamate	4	
		940	
30	40 parts by weight of a 10% solution of beta-cyclohomocitral (prepared according to the process of Example XXIV) in diethyl phthalate is added to the above formulation. The beta-cyclohomocitral improves the floral nuance of this formulation by significantly increasing the rosey character of this muguet fragrance.		30
35	In another experiment, 80 parts by weight of a 10% solution of beta-cyclohomocitral (prepared according to the process of Example XXIV) in diethyl phthalate is added to the above muguet formulation. The beta-cyclohomocitral markedly improves the floral nuance of the compound by increasing, significantly, its rosey character.		35

### EXAMPLE XXVI. FLORAL PERFUME FORMULATION

The following floral formulation is prepared:

	Ingredients	Parts by Weight	
5	Lavendar Barreme	60	5
	Linalool	370	
	Phenyl Ethyl Alcohol	500	
	Benzyl acetate	120	
	Linalyl Acetate	520	
10	Hydroxy Citronellal	600	10
	4(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde	100	
	Eugenol	230	
	Alpha isomethyl ionone	1000	
15	Sandalwood Oil	120	15
	Ylang Oil	50	
	Musk Ambrette	100	
	Benzyl Salicylate	1350	
20	6-oxa-1,2,3,3,8-hexamethyl-2,3,5,6,7,8-hexahydro-1H-Benze[f]-indene prepared according to the process of Example XV of U.S. patent 3,360,530 (50% in diethyl phthalate)	550	20
	4'-t-butyl-2',6'-dimethyl-3',5'-dinitro acetophenone	450	
25	p-t-butyl-alpha-methyl-hydrocinnamic aldehyde	20	25
	diethyl phthalate	90	
		6230	

30 35 parts by weight of a 10% solution (diethyl phthalate) of beta-cyclohomocitral (prepared according to the process of Example XXIV) is added to this formulation. The beta-cyclohomocitral creates a rosey effect in this floral form-  
 30 another 35 parts by weight of 10% (in diethyl phthalate) of beta-cyclohomocitral. The rosey effect is further improved slightly by addition of another 35 parts by weight of 10% (in diethyl phthalate) of beta-cyclohomocitral produced according to Example XXIV.  
 35

### EXAMPLE XXVII.

#### PREPARATION OF A SOAP COMPOSITION

40 100 grams of soap chips are mixed with one gram of the perfume composition of Example XXV until a substantial homogeneous composition is obtained. The perfumed soap composition manifests an excellent muguet character with excellent floral notes.  
 40

### EXAMPLE XXVIII.

#### PREPARATION OF A DETERGENT COMPOSITION

45 A total of 100 grams of detergent powder is mixed with 0.15 grams of the perfume composition of Example XXV, until a substantially homogeneous composition is obtained. This composition has an excellent muguet aroma with floral notes.  
 45

## EXAMPLE XXIX.

## PREPARATION OF A COLOGNE AND HANDKERCHIEF PERFUME

The composition of Example XXVI is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume a concentration of 20% (in 95% aqueous ethanol). A distinct and definite strong rosey aroma is imparted to the cologne and to the handkerchief perfume.

## EXAMPLE XXX.

## ROSE FRAGRANCE

The following rose formulation is prepared:

10	Ingredients	Parts by Weight	10
	Rhodinol	270.0	
	Nerol	90.0	
	Linalool	30.0	
	Terpineol	30.0	
15	Phenyl ethyl alcohol	12.0	15
	Terpinenol	5.0	
	Linalyl acetate	1.5	
	Citronellyl acetate	15.0	
	Geranyl acetate	10.0	
20	Eugenol	30.0	20
	Citral	15.0	
	Phenyl ethyl acetate	20.0	
	Rose Oxide	8.0	
	Guaicol	30.0	
25	Citronellyl	93.0	25
	Neryl acetate	3.0	
	Clove bud oil	1.0	
	Cadinene	2.0	
	Guaiene	1.0	
30	French gum turpentine	12.0	30
	Alpha pinene	1.0	
	Myrcene purified	5.0	
	Limonene	2.0	
	p-cymene	1.0	
35		687.5	35

30 parts by weight of a 0.1% solution of beta-cyclohomocitral (in diethyl phthalate) is added to a portion of the foregoing formulation. The formulation which contains the beta-cyclohomocitral is a much brighter rose top note as compared to the formulation without said beta-cyclohomocitral.

5

## EXAMPLE XXXI.

5

## PREPARATION OF A SOAP COMPOSITION

100 grams of soap chips are mixed with 1 gram of the perfume composition of Example XXX, until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent rose character.

10

## EXAMPLE XXXII.

10

## PREPARATION OF A DETERGENT COMPOSITION

A total of 100 grams of detergent powder is mixed with 0.15 grams of the perfumed composition of Example XXX until a substantially homogeneous composition is obtained. This composition has an excellent rose aroma.

15

## EXAMPLE XXXIII.

15

## PREPARATION OF A COSMETIC POWDER COMPOSITION

A cosmetic powder is prepared by mixing in a ball mill, 100 grams of talcum powder with 0.25 grams of the perfumed formulation of Example XXX. The resulting powder has an excellent rosey aroma.

20

## EXAMPLE XXXIV.

20

## RASPBERRY FLAVOR FORMULATION

The following basic raspberry flavor formulation is produced:

Ingredient	Parts by Weight	
Vanillin	2.0	
Maltol	5.0	25
Parahydroxybenzylacetone	5.0	
Alpha-ionone (10% in propylene glycol)	2.0	
Ethyl Butyrate	6.0	
Ethyl Acetate	16.0	
Dimethyl Sulfide	1.0	30
Isobutyl Acetate	13.0	
Acetic Acid	10.0	
Acetaldehyde	10.0	
Propylene Glycol	930.0	

35

Beta-cyclohomocitral is added to half of the above formulation at the rate of 0.2%. The formulation with the beta-cyclohomocitral is compared with the formulation without the beta-cyclohomocitral at the rate of 0.01 percent (100 ppm) in water and evaluated by a bench panel.

35

40

The flavor containing the beta-cyclohomocitral is found to have a substantially more pleasant and better raspberry aroma. It is the unanimous opinion of the bench panel that the chemical, beta-cyclohomocitral rounds the flavor out and contributes to a very natural fresh aroma and taste as found in full ripe raspberries. Accordingly, the flavor with the addition of the beta-cyclohomocitral is considered as substantially better than the flavor without beta-cyclohomocitral.

40



## EXAMPLE XXXV.

## TOBACCO FORMULATION

A tobacco mixture is produced by admixing the following ingredients:

	Ingredient	Parts by Weight	
5	Bright	40.1	5
	Burley	24.9	
	Maryland	1.1	
	Turkish	11.6	
	Stem (flue-cured)	14.2	
10	Glycerine	2.8	10
	Water	5.3	

Cigarettes are prepared from this tobacco.

The following flavor formulation is prepared:

	Ingredient	Parts by Weight	
15	Ethyl butyrate	.05	15
	Ethyl valerate	.05	
	Maltol	2.00	
	Cocoa extract	26.00	
	Coffee extract	10.00	
20	Ethyl alcohol	20.00	20
	Water	41.90	

The above-stated tobacco flavor formulation is applied at the rate of 0.1% to all of the cigarettes producing using the above tobacco formulation. Half of the cigarettes are then treated with 500 or 1,000 ppm of beta-cyclohomocitral produced according to the process of Example I or XVI. The control cigarettes not containing the beta-cyclohomocitral produced according to the process of Example I or XVI and the experimental cigarettes which contain the beta-cyclohomocitral produced according to the process of Example I or XVI are evaluated by paired comparison and the results are as follows:

The experimental cigarettes are found to have more body and to be, on smoking, sweeter, richer, more tobacco-like and less harsh with woody, damascenone-like notes.

The tobacco of the experimental cigarettes, prior to smoking, has sweet, floral, fruity, earthy and green notes. All cigarettes are evaluated for smoke flavor with a 20 mm cellulose acetate filter.

The beta-cyclohomocitral produced according to the process of Example I or XVI enhances the tobacco-like taste and aroma of the blended cigarette imparting to it woody, damascenone-like notes.

EXAMPLE XXXVI.  
RASPBERRY FLAVOR FORMULATION

The following formulation is prepared:

	Ingredients	Parts	
5	Vanillin	2	5
	Maltol	4	
	Para-Hydroxybenzylacetone	5	
	Alpha-Ionone (10% in propylene glycol)	2	
	Ethyl butyrate	6	
10	Ethyl acetate	16	10
	Dimethyl sulfide	1	
	Isobutyl acetate	14	
	Acetic acid	10	
	Acetaldehyde	10	
15	Propylene glycol	930	15
		1000	

To each of three portions of the foregoing formulation one of the following compositions of matter is added:

- 20 a. damascenone at 0.01 ppm;  
b. beta-cyclohomocitral at 0.1 ppm;  
c. mixture of damascenone at 0.01 ppm and beta-cyclohomocitral at 0.1 ppm. 20

25 The mixture of damascenone and beta-cyclohomocitral as such is sweeter, fruitier, fruity/rosey and more pleasant in taste and aroma than the beta-cyclohomocitral or the damascenone taken alone when examined in ethanol solutions at a concentration of 10%.

25 At the indicated levels in the above-mentioned raspberry formulation the three compositions of matter are compared at 100 ppm in water by members of a bench panel. A majority of the members of the bench panel preferred the flavor formulation containing the mixture of damascenone and beta-cyclohomocitral as being the most natural raspberry flavor since it is the only composition of matter 30 than has the characteristic seedy note of ripe raspberries.

30 Addition of the mixture of damascenone and beta-cyclohomocitral to the flavor formulation gives rise to an unexpected effect since only 50% of each of the ingredients of the mixture is required to yield the same strength taste and aroma notes as could be expected by merely testing organoleptically the original 35 compounds by themselves.

Similar results are achieved using the following weight ratios of damascenone to beta-cyclohomocitral:

	ppm damascenone	ppm-beta-cyclohomocitral	weight ratio	
40	0.05	1.0	1:20	
	0.15	1.0	1:6.7	40
	0.20	1.0	1:5	
	0.25	1.0	1:4	
	0.4	1.0	1:2.5	
45	0.6	1.0	1:1.7	45
	1.0	1.0	1:1	

## EXAMPLE XXXVII.

## ROSE FORMULATION

The following mixture is prepared:

	Ingredients	Parts by Weight	
5	Rhodinol	270.0	5
	Nerol	90.0	
	Linalool	30.0	
	Terpineol	30.0	
	Phenyl Ethyl Alcohol	12.0	
10	Terpinenol	5.0	10
	Linalyl Acetate	1.5	
	Citronellyl Acetate	15.0	
	Geranyl Acetate	10.0	
	Eugenol	33.0	
15	Citral	15.0	15
	Phenyl Ethyl Acetate	20.0	
	Rose Oxide	8.0	
	Guaiacol	30.0	
	l-citronellal	90.0	
20	Neryl Acetate	3.0	20
	Clove Bud Oil	1.0	
	Cadinene	2.0	
	Guaiene	1.0	
	Gum Turpentine	12.0	
25	Alpha-pinene	1.0	25
	Myrcene	5.0	
	Limonene	2.0	
	p-cimene	1.0	
		687.5	

30 To the foregoing formulation 30 parts by weight of a 0.1% solution of beta-cyclohomocitral in diethyl phthalate and 15 parts by weight of an 0.01% solution of damascenone in diethyl phthalate is added. The resultant mixture has a much brighter rose top note and is fruitier and richer on dry out as compared with the same mixture without the composition of matter containing the beta-cyclo-

35 homocitral and the damascenone.

EXAMPLE XXXVIII.  
PREPARATION OF A SOAP COMPOSITION

5 100 Grams of soap chips are mixed with one gram of the perfume composition of Example XXXVII until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent fruity, rose character with green, earthy notes. 5

EXAMPLE XXXIX.  
PREPARATION OF A DETERGENT COMPOSITION

10 A total of 100 grams of detergent powder is mixed with 0.15 grams of the perfume composition of Example XXXVII until a substantially homogeneous composition is obtained. This composition has an excellent fruity, rose aroma with earthy, green notes. 10

EXAMPLE XL.  
PERFUMED LIQUID DETERGENT

15 Concentrated liquid detergent each with a fruity, rosey aroma are prepared containing 0.10%, 0.15% and 0.20% of a mixture of damascenone and beta-cyclohomocitral in a weight ratio of 1:0.1 of beta-cyclohomocitral:damascenone. They are prepared by adding and homogeneously mixing the appropriate quantity of a mixture of damascenone and beta-cyclohomocitral in the liquid detergent. The detergents all possess a fruity, rosey fragrance, the intensity increasing with greater concentrations of mixture of damascenone and beta-cyclohomocitral. 15  
20

EXAMPLE XLI.  
PREPARATION OF A COLOGNE AND HANDKERCHIEF PERFUME

25 The composition of Example XXXVII is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). The use of the mixture of damascenone and beta-cyclohomocitral in the composition of Example XXXVII affords a distinct and definite strong fruity, rose aroma with earthy and green notes to the handkerchief perfume and cologne. 25

EXAMPLE XLII.  
PREPARATION OF SOAP COMPOSITION

30 100 Grams of soap chips are mixed with 1 gram of a mixture of damascenone and beta-cyclohomocitral where the ratio of damascenone:beta-cyclohomocitral is 0.1:1, until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent rose aroma with woody, green and earthy notes and an excellent sweet top note. 30  
35

EXAMPLE XLIII.  
PREPARATION OF A DETERGENT COMPOSITION

40 A total of 100 g of a detergent powder is mixed with 0.15 g of a mixture of damascenone and beta-cyclohomocitral (the ratio of damascenone:beta-cyclohomocitral being 0.2:1) until a substantially homogeneous composition is obtained. This composition has an excellent rose aroma with woody, green and earthy notes. 40

EXAMPLE XLIV.  
PREPARATION OF A COLOGNE AND HANDKERCHIEF PERFUME

45 A mixture of 1 part beta-cyclohomocitral and 2 parts damascenone is incorporated into a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). A distinct and definite rose fragrance with woody, green and earthy top notes is imparted to the cologne and to the handkerchief perfume. 45  
50

EXAMPLE XLV.  
PREPARATION OF A COSMETIC-POWDER COMPOSITION

55 A cosmetic powder is prepared by mixing in a ball mill, 100 grams of talcum powder with 0.15 grams of a mixture consisting of 50% beta-cyclohomocitral and 50% damascenone. It has an excellent rose aroma with woody, green and earthy notes. 55

EXAMPLE XLVI.  
TOBACCO FORMULATION

A tobacco mixture is produced by admixing the following ingredients:

	Ingredient	Parts by Weight	
5	Bright	40.1	5
	Burley	24.9	
	Maryland	1.1	
	Turkish	11.6	
	Stem (flue-cured)	14.2	
10	Glycerine	2.8	10
	Water	5.3	

Cigarettes are prepared from this tobacco.

The following flavor formulation is prepared:

	Ingredient	Parts by Weight	
15	Ethyl butyrate	.05	15
	Ethyl valerate	.05	
	Maltol	2.00	
	Cocoa extract	26.00	
	Coffee extract	10.00	
20	Ethyl alcohol	20.00	20
	Water	41.90	

The above-stated tobacco flavor formulation is applied at the rate of 0.1% to all of the cigarettes produced using the above tobacco formulation. Half of the cigarettes are then treated with 250 or 500 ppm of a mixture containing 0.1 parts damascenone and one part beta-cyclohomocitral. The control cigarettes not containing this composition of matter containing damascenone and beta-cyclohomocitral and the experimental cigarettes which contain the damascenone and beta-cyclohomocitral are evaluated by paired comparison and the results are set forth as follows:

The experimental cigarettes are found to have more body and thereby, on smoking, sweeter, richer, more tobacco-like and less harsh with intense woody and fruity notes.

The tobacco of the experimental cigarettes, prior to smoking, has sweet, rosey, floral, fruity, earthy and green notes. All cigarettes are evaluated for smoke flavor with a 20 mm cellulose acetate filter.

The mixture of beta-cyclohomocitral and damascenone enhances the natural tobacco-like taste and aroma of a blended cigarette imparting to it the woody and fruity notes on smoking.

EXAMPLE XLVII.

2 ppm of a 1:1 mixture of damascenone and beta-cyclohomocitral are added to burgundy red wine, ("Selected California" produced by the Christian Brothers of Napa, California) and compared with an unflavored wine by a bench panel. The wine flavored with the mixture of damascenone and beta-cyclohomocitral is

preferred as having more top notes and a richer aroma, giving the effect of "round" and "aged" wine.

#### EXAMPLE XLVIII.

5 A mixture containing 3 parts by weight beta-cyclohomocitral and 1 part by weight of damascenone is added to distilled white vinegar at the rate of 0.01% and compared in water at the rate of 1% with the unflavored vinegar. The mixture of damascenone and beta-cyclohomocitral adds natural-like, wine vinegar-like top notes to the distilled white vinegar and rounds off the top notes thus improving the aroma and taste of this product.

#### EXAMPLE XLIX.

##### (A) POWDER FLAVOR

10 20 Grams of the flavor composition of Example XXXVI which flavor composition contains a mixture of beta-cyclohomocitral and damascenone, is emulsified in a solution containing 300 gm gum acacia and 700 gm water. The emulsion is spray-dried with a Bowen Lab Model Drier utilizing 250 c.f.m. of air with an inlet temperature of 500°F., and outlet temperature of 200°F., and a wheel speed of 50,000 r.p.m.

##### (B) PASTE BLEND

The following mixture is then prepared:

20	Ingredient	Parts by Weight	20
	Liquid Flavor Composition of Example XXXVI	48.4	
	Cab-O-Sil®M—5 (Brand of Silica produced by the Cabot Corporation of 125 High Street, Boston, Mass. 02110; Physical Properties:	3.2	
25	Surface Area: 200 m <sup>2</sup> /gm Nominal Particle Size: 0.012 microns Density: 2/3 lbs/cu.ft.		25

30 The Cab-O-Sil is dispersed in any of the exemplified liquid flavor compositions with vigorous stirring, thereby resulting in a viscous liquid. 48.4 Parts by weight of the powder flavor composition prepared in Part A is then blended into the said viscous liquid, with stirring at 25°C for a period of 30 minutes, resulting in a thixotropic sustained release flavor paste.

#### EXAMPLE L. CHEWING GUM

35 100 Parts by weight of chicle are mixed with 4 parts by weight of the flavor prepared in accordance with Example XLIX. 300 Parts of sucrose and 100 parts of corn syrup are added. Mixing is effected in a ribbon blender with jacketed side walls of the type manufactured by the Baker Perkins Co.

40 The resultant chewing gum blend is then manufactured into strips 1 inch in width and 0.1 inches in thickness. The strips are cut into lengths of 3 inches each. On chewing the chewing gum has a pleasant long lasting raspberry flavor.

## EXAMPLE LI.

## TOOTHPASTE FORMULATION

The following separate groups of ingredients are prepared:

	Group "A"		
5	30.200	Glycerin	5
	15.325	Distilled Water	
	.100	Sodium Benzoate	
	.125	Saccharin Sodium	
	.400	Stannous Fluoride	
10	Group "B"		10
	12.500	Calcium Carbonate	
	37.200	Dicalcium Phosphate (Dihydrate)	
	Group "C"		
15	2.000	Sodium N-Lauroyl Sarcosinate (Foaming Agent).	15
	Group "D"		
	1.200	Flavor Material of Example XLIX	
	100.00 (Total)		

## PROCEDURE

- 20 1. The ingredients in Group "A" are stirred and heated in a steam jacketed kettle to 160°F. 20
2. Stirring is continued for an additional three to five minutes to form a homogenous gel.
- 25 3. The powders of Group "B" are added to the gel, while mixing until a homogenous paste is formed. 25
4. With stirring, the flavour of "D" is added and lastly the sodium n-lauroyl sarcosinate.
5. The resultant slurry is then blended for one hour. The completed paste is then transferred to a three roller mill and then homogenized, and finally tubed.
- 30 The resulting toothpaste when used in a normal tooth-brushing procedure yields a pleasant raspberry flavour, of constant strong intensity throughout said procedure (1—1.5 minutes). 30

## EXAMPLE LII.

## CHEWABLE VITAMIN TABLETS

- 35 The flavour material produced according to the process of Example XIV is added to a Chewable Vitamin Tablet Formulation at a rate of 5 gm/gm which Chewable Vitamin Tablet Formulation is prepared as follows: 35

		Gms/1000 tablets	
	Vitamin C (ascorbic acid) as ascorbic acid-sodium ascorbate mixture 1:1	70.0	
5	Vitamin B <sub>1</sub> (thiamine mononitrate) as Rocoat thiamine mononitrate 33 1/3% (Hoffman La Roche)	4.0	5
	Vitamin B <sub>2</sub> (riboflavin) as Rocoat riboflavin 33 1/3%	5.0	
10	Vitamin B <sub>6</sub> (pyridoxine hydrochloride) as Rocoat pyridoxine hydrochloride 33 1/3%	4.0	10
	Niacinamide as Rocoat niacinamide 33 1/3%	33.0	
	Calcium pantothenate	11.5	
15	Vitamin B <sub>12</sub> (Cyanocobalamin) as Merk 0.1% in gelatin	3.5	15
	Vitamin E (dl-alpha tocopheryl acetate) as dry Vitamin E acetate 33 1/3% Roche	6.6	
	d-Biotin	0.044	
20	Certified lake colour	5.0	20
	Flavour of Example XLIX	5.0	
	Sweetener — sodium saccharin	1.0	
	Magnesium stearate lubricant	10.0	
	Mannitol q.s. to make	500.0	
25	Preliminary tablets are prepared by slugging with flat-faced punches and grinding the slugs to 14 mesh. 13.5 g dry Vitamin A Acetate and 0.6 g Vitamin D are then added as beadlets. The entire blend is then compressed using concave punches at 0.5 g each.		25
30	Chewing of the resultant tablet yields a pleasant, long-lasting, consistently strong raspberry flavour for a period.		30

## EXAMPLE LIII.

## ROSE ESSENCES

The following formulation is prepared:

	Ingredient	Parts by Weight	
35	Phenyl Ethyl Alcohol	1040	35
	Geraniol	390	
	Citronellol	390	
	Alpha Ionone	130	
	Hydroxy Citronellal	130	
40		2080	40



(A) In a first experiment 208 parts of "Damascol-4" (2,5-dimeth 1-5-phenyl-hexanone-3) is added to this formulation.

(B) In a second experiment, 208 parts of "Damascol-4" and 52 parts of 10% beta-cyclohomocitral in diethyl phthalate are added to this formulation.

(C) In a third experiment, 104 parts of "Damascol-4" and 52 parts of 10% beta-cyclohomocitral in diethyl phthalate is added to this formulation.

(D) In a fourth experiment, 208 parts of "Damascol" (2,5-dimethyl-5-phenylhexen-1-one-3) is added to the above formulation.

(E) In a fifth experiment, 208 parts of "Damascol" and 52 parts beta-cyclohomocitral is added to the formulation.

(F) In a sixth experiment, 104 parts of "Damascol" and 52 parts 10% beta-cyclohomocitral in diethyl phthalate is added to the formulation.

The beta-cyclohomocitral significantly improves the rosiness of the formulation when used with the "Damascol-4", in Experiments "B" and "C".

The combination of the beta-cyclohomocitral and "Damascol" significantly improves the rosiness of the formulation in Experiments "E" and "F".

#### EXAMPLE LIV.

##### PREPARATION OF A SOAP COMPOSITION

100 Grams of soap chips are mixed with one gram of the perfume composition of Example LIII (Experiment B) until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent rose character.

#### EXAMPLE LV.

##### PREPARATION OF A DETERGENT COMPOSITION

A total of 100 grams of detergent powder is mixed with 0.15 grams of the perfume composition of Example LIII (Experiment C) until a substantially homogeneous composition is obtained. This composition has an excellent rose aroma.

#### EXAMPLE LVI.

##### PERFUMED LIQUID DETERGENT

Concentrated liquid detergents with a rosey aroma and woody, green and earthy nuances are prepared containing 0.10%, 0.15% and 0.20% of a mixture of beta-cyclohomocitral and damascol having a weight ratio of 2 parts damascol:1 part beta-cyclohomocitral. They are prepared by adding and homogeneously mixing the appropriate quantity of damascol-beta-cyclohomocitral mixture in the liquid detergent. The detergents all possess an excellent rose fragrance, with woody, green and earthy notes, the intensity increasing with greater concentrations of damascol-beta-cyclohomocitral mixture.

#### EXAMPLE LVII.

##### PREPARATION OF A COLOGNE AND HANDKERCHIEF PERFUME

A mixture of damascol and beta-cyclohomocitral (weight ratio: 2 parts damascol:1 part beta-cyclohomocitral) is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). A distinct and definite rosey fragrance with woody, green and earthy notes is imparted to the cologne and to the handkerchief perfume.

#### EXAMPLE LVIII.

##### PREPARATION OF A COLOGNE AND HANDKERCHIEF PERFUME

The composition of Example LIII (Experiment E) is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). The use of the damascol-beta-cyclohomocitral mixture in the composition of Example LIII (Experiment E) affords a distinct and definite strong rose aroma to the handkerchief perfume and cologne.

#### EXAMPLE LIX.

##### PREPARATION OF SOAP COMPOSITION

One hundred grams of soap chips are mixed with one gram of a mixture of beta-cyclohomocitral and "Damascol-4" (ratio of beta-cyclohomocitral:4-damascol is 1:3) until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent rose aroma with woody, green and earthy nuances.

## EXAMPLE LX.

## PREPARATION OF A DETERGENT COMPOSITION

A total of 100 g of a detergent powder is mixed with 0.15 g of the mixture of beta-cyclohomocitral and "Damascol-4" (ratio of beta-cyclohomocitral:4-damascol is 1:4) until a substantially homogeneous composition is obtained. This composition has an excellent rose aroma with woody, green and earthy nuances.

## EXAMPLE LXI.

## PREPARATION OF A SOAP COMPOSITION

100 Grams of soap chips are mixed with one gram of the perfume composition of Example LIII (Experiment F) until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent rose character.

## EXAMPLE LXII.

## PREPARATION OF A DETERGENT COMPOSITION

A total of 100 grams of detergent powder is mixed with 0.15 grams of the perfume composition of Example LIII (Experiment F) until a substantially homogeneous composition is obtained. This composition has an excellent rose aroma.

## EXAMPLE LXIII.

## PERFUMED LIQUID DETERGENT

Concentrated liquid detergents with long-lasting, strong rose fragrance having woody, green and earthy notes are prepared containing 0.10%, 0.15% and 0.20% of a 1:1 damascol:beta-cyclohomocitral mixture. They are prepared by adding and homogeneously mixing the appropriate quantity of beta-cyclohomocitral-damascol mixture in the liquid detergent. The detergents all possess a rose aroma with woody, green and earthy notes, the intensity increasing with greater concentrations of beta-cyclohomocitral-damascol mixture.

## EXAMPLE LXIV.

## PREPARATION OF A COLOGNE AND HANDKERCHIEF PERFUME

A 1:1 4-damascol-beta-cyclohomocitral mixture is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). A distinct and definite rose fragrance with woody, green and earthy notes is imparted to the cologne and to the handkerchief perfume.

## EXAMPLE LXV.

## PREPARATION OF A COLOGNE AND HANDKERCHIEF PERFUME

The composition of Example LIII (Experiment F) is incorporated in a cologne at a concentration of 2.5% in 85% aqueous ethanol; and into a handkerchief perfume at a concentration of 20% (in 95% aqueous ethanol). The use of the damascol-beta-cyclohomocitral mixture in the composition of Example LIII affords a distinct and definite strong rose aroma to the handkerchief perfume and cologne.

## EXAMPLE LXVI.

## PREPARATION OF SOAP COMPOSITION

One hundred grams of soap chips are mixed with one gram of a 1:1 4-damascol:beta-cyclohomocitral mixture until a substantially homogeneous composition is obtained. The perfumed soap composition manifests an excellent rose aroma with woody, green and earthy nuances.

## EXAMPLE LXVII.

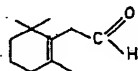
## PREPARATION OF A DETERGENT COMPOSITION

A total of 100 g of a detergent powder is mixed with 0.15 g of a 1:1 4-damascol:beta-cyclohomocitral mixture until a substantially homogeneous composition is obtained. This composition has an excellent rose aroma with woody, green and earthy nuances.

## WHAT WE CLAIM IS:—

1. A process for altering, modifying or enhancing the organoleptic properties of a consumable material selected from the group consisting of perfume compositions, perfumed articles, food flavoring compositions, foodstuffs, tobacco

flavoring compositions and tobacco which comprises adding thereto a small but effective amount of an organoleptic property modifying, enhancing, altering or imparting composition comprising 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde having the structure:



2. A process according to Claim 1 wherein the consumable material is a foodstuff.

3. A process according to Claim 1 wherein the consumable material is a perfumed article selected from the group consisting of a soap, detergent and cosmetic powder.

4. A process according to Claim 1 wherein the consumable material is a tobacco.

5. A process according to Claim 1 wherein the consumable material is a food flavor.

6. A flavor modifying composition suitable for use in the process of any one of Claims 2 to 5 comprising 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde and as a flavor adjuvant, a compound selected from the group consisting of p-hydroxybenzyl acetone, maltol, benzyl acetate, methyl cinnamate, geraniol, ethyl methyl phenyl glycidate, vanillin, methyl anthranilate, alpha-ionone, gamma undecalactone, ethyl pelargonate, isoamyl acetate, acetaldehyde, dimethyl sulfide, osobutyl acetate, acetic acid, ethyl butyrate, diacetyl, anethole, cis-3-hexenol-1, naphthyl ethyl ether, ethyl acetate, isoamyl butyrate, 2-methyl-2-pentenoic acid, 2-(4-hydroxy-4-methylpentyl) norbornadiene, 4-allyl-1,2,6-trimethoxy benzene and 4-propenyl-1, 2,6-trimethoxy benzene.

7. A fragrance modifying composition suitable for use in the process of Claim 3 or 4 comprising 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde and an auxiliary perfume ingredient compatible with said 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde.

8. A perfume composition suitable for use in the process of Claim 3 comprising 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde and at least one adjuvant selected from the group consisting of natural perfume oil, synthetic perfume oil, alcohols, aldehydes, ketones, esters and lactones.

9. A perfumed article comprising 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde and a detergent, soap, cosmetic preparation or powder.

10. A process for producing a perfumed composition comprising the step of admixing a composition of matter with a fragrance imparting amount of 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde.

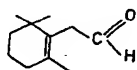
11. A cologne composition comprising ethanol, water and 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde.

12. A tobacco flavoring composition comprising 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde and as a flavor adjuvant a compound selected from the group consisting of ethyl butyrate, ethyl valerate and maltol.

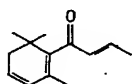
13. A process for altering the organoleptic properties of a consumable material selected from the group consisting of perfume compositions, perfumed articles, food flavoring compositions, foodstuffs, tobacco flavoring compositions and tobacco which comprises adding thereto a small but effective amount of 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde.

14. A process according to claim 13 wherein the consumable material is a foodstuff.

15. The process for altering, modifying or enhancing the organoleptic properties of a consumable material of Claim 1 wherein the organoleptic property-modifying, enhancing, altering or imparting composition comprises a mixture consisting essentially of 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde having the structure:



and 2,6,6-trimethyl-1-1-crotonyl-1,3-cyclohexadiene having the structure:



16. A flavor modifying composition of Claim 6 further comprising 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene.

17. A fragrance modifying composition of Claim 7 further comprising 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene, the auxiliary perfume ingredient being also compatible with said 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene.

18. A perfume composition of Claim 8 further comprising 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene.

19. A perfume article of Claim 9 further comprising 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene.

20. A process for producing a perfumed composition comprising the step of admixing a composition of matter having an aroma impression capable of being naturally altered, modified or enhanced with a fragrance imparting amount of the mixture of claim 17.

21. The cologne composition of Claim 11 further comprising 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene.

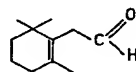
22. The tobacco flavoring composition of Claim 12 further comprising 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene.

23. A composition of matter consisting essentially of 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde and 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene.

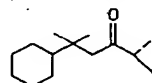
24. The composition of matter of Claim 23 wherein the weight ratio of 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde and 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene is in the range of from 1:20 to 1:1.

25. The composition of matter of Claim 23 wherein the weight ratio of 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde and 2,6,6-trimethyl-1-crotonyl-1,3-cyclohexadiene is in the range of from 1:20 up to 1:10.

26. A mixture suitable for use in the process of Claim 1 consisting essentially of (i) 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde having the structure:



and (ii) a phenyl C<sub>6</sub> ketone having the structure:



wherein the dashed line represents a carbon-carbon single bond or a carbon-carbon double bond; the weight ratio of said 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde:phenyl C<sub>6</sub> ketone being in the range of from about 1:1 up to about 1:5.

27. A process for altering the organoleptic properties of a consumable material selected from the group consisting of perfume compositions and perfumed articles, which comprises adding thereto a small but effective amount of the composition of Claim 26.

28. A process according to Claim 27 wherein the consumable material is a perfumed article selected from the group consisting of a soap, detergent and cosmetic powder.

29. A fragrance modifying composition comprising (i) the mixture of Claim 26 and (ii) an auxiliary perfume ingredient compatible with said 2,6,6-trimethyl-1-cyclohexen-1-ylacetaldehyde.

30. A perfume composition comprising (i) the mixture of Claim 26 and (ii) at least one adjuvant selected from the group consisting of natural perfume oil, synthetic perfume oil, alcohols, aldehydes, ketones, esters and lactones.

31. A perfume article comprising (i) the mixture of Claim 26 and (ii) a detergent, soap, cosmetic preparation or powder.

32. A process for producing a perfumed composition comprising the step of admixing a composition of matter having an aroma impression capable of being altered or modified or enhanced whereby said composition of matter retains a definitive rose note with a fragrance imparting amount of the mixture of Claim 26.

33. A cologne comprising (i) ethanol, (ii) water and (iii) the mixture of Claim 26.

34. A composition for flavoring foodstuffs as claimed in any one of Claims 6 and 16 substantially as herein described with reference to any one of Examples XXXIV, XXXVI, XLVII and XLVIII.

35. A composition for flavoring tobacco as claimed in claims 12 and 22 substantially as herein described with reference to any one of Examples XLVI and XXXV.

36. A fragrance modifying, altering or enhancing composition as claimed in Claims 7, 8, 17, 18, 29 and 30 substantially as herein described with reference to any one of Examples XI, XXV, XXVI, XXX, XXXVII and LIII.

37. A cologne composition as claimed in Claims 11, 21 and 33 substantially as herein described with reference to Examples XIX, XX, XXIX, XLI, XLIV, LVIII, LXIV, and LXV.

38. A perfumed article as claimed in Claims 9, 19 and 31 substantially as herein described with reference to Examples XII, XIII, XVII, XVIII, XXI, XXII, XXVII, XXVIII, XXXI, XXXII, XXXIII, XXXVII, XXXIX, XL, XLII, XLIII, XLV, LIV, LV, LVI, LIX, LX, LXI, LXII, LXIII, LXVI and LXVII.

39. An organoleptic property modifying or altering or enhancing composition as claimed in Claims 6, 7, 8, 11, 12, 16, 17, 18, 22, 29, 30 and 33 substantially as herein described with reference to any one of Examples XI—XIII, XVII—XXII, XXV—XXXV, XXXVI—LII and LIII—LXIII.

40. A process for altering the organoleptic properties of a consumable material which is one of a perfume composition, a perfumed article, a food flavoring composition, a foodstuff, a chewing gum flavoring composition, a chewing gum, a medicinal produce flavoring composition, medicinal product, a tobacco flavoring composition or a tobacco of any one of claims 1—5, 10, 13—15, 20, 27, 28 or 32 substantially as herein described with reference to any of Examples XI—XIII, XVII—XXII, XXV—XXXV, XXXVI—LII and LIII—LXIII.

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